

Chemical composition of rainwater in Panipat, an industrial city in Haryana

S Tiwari^{1,§,*}, Manoj K Srivastava² & Deewan Singh Bisht¹

¹Indian Institute of Tropical Meteorology, New Delhi Branch, New Rajinder Nagar, New Delhi 110 060, India

²Department of Geophysics, Banaras Hindu University, Varanasi 221 005, India

[§]Email: smbtiwari@yahoo.co.uk

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Chemical composition of rainwater at Panipat, an industrial city in India, during the south-west monsoon seasons 2003-2005 has been studied. The collected samples have been analyzed for major anions, cations and pH along with conductivity. The volume weighted pH of rainwater varied from 5.02 to 6.86 with a mean value of 5.51, which is slightly acidic. About 37% of rain samples were observed to be acidic due to high SO₂ emissions from industries. The trend of average ionic concentration in precipitation (µeq/l) showed SO₄²⁻ > Ca²⁺ > NH₄⁺ > Cl⁻ > NO₃⁻ > Na⁺ > Mg²⁺ > F⁻ > K⁺ > HCO₃⁻. The percentage contribution to the total ionic concentration is found to be 51% to cations and 49% to anions. Sulphate, calcium and ammonium shared maximum contribution. Major part of sulphate ion in rainwater at Panipat was of anthropogenic origin, i.e. by the oxidation of sulphur dioxide emitted from burning of fossil fuels from thermal power plant, oil refinery, fertilizer plant, etc. The major source of nitrate was biomass burning, automobile and soil. Ammonium in precipitation was due to bacterial action on nitrogen compounds in the soil, urine and from industrial sources. The ratio of sea salt (Na⁺ and Cl⁻) was equal to the seawater, suggesting that it was mostly influenced by marine air.

Keywords: Rainwater chemistry, Ion concentration

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1 Introduction

Several studies in precipitation chemistry have been done in recent years because of awareness of the impact on the ecosystem by acid rain particularly on human health¹. Rainwater chemistry also enables to understand the relative importance of different sources of gaseous and particulate pollutants, which have been the subject of immense research in Europe, USA and other parts of the world for the last 30 years²⁻⁷. Rainwater chemistry in urban areas is attributed to the local pollution sources, whereas in remote and rural areas, it provides the extent of impact of anthropogenic and natural sources.

Studies in urban and rural regions in India⁸⁻¹³ pointed out both man-made and natural pollutants (dust particles) with significant base cations influencing the rainwater chemistry. The acidity of rainwater is completely neutralized by cations prior to its fall on the ground surface. Considering the importance of chemical transformations in polluted atmosphere as well as in precipitation, studies on rainwater chemistry were undertaken during the south-west monsoon season 2003-2005 at Panipat, an industrialized city in the state of Haryana in India.

2 Experimental set up

2.1 Site description

Panipat (29.25°N, 77.02°E) is about 1100 km away from the nearest coast of Arabian Sea and 90 km to the north of Delhi. Three large industries (thermal power station, fertilizer plant and an oil refinery) besides 34 medium and 2898 small-scale industries (textile, chemical, paper mill, dyeing, processing units, handloom, etc.) are located there. Sampling site was at Babarpur, a small village 5 km away from Panipat to the North (Fig. 1).

2.2 Sample collection

Rainwater samples were collected on event basis with a rain collector placed about 10 m above ground. The bottles as well as funnels in the collector were cleaned by triple distilled water twice daily in the morning and evening to avoid dry deposition of gaseous and particulate species. Collected samples were then stored in small polythene bottles, also cleaned by triple distilled water and adding Thymol (< 2mg) for preventing biological degradation of the samples. All samples were refrigerated at 4°C in the laboratory till all ionic components were analyzed.

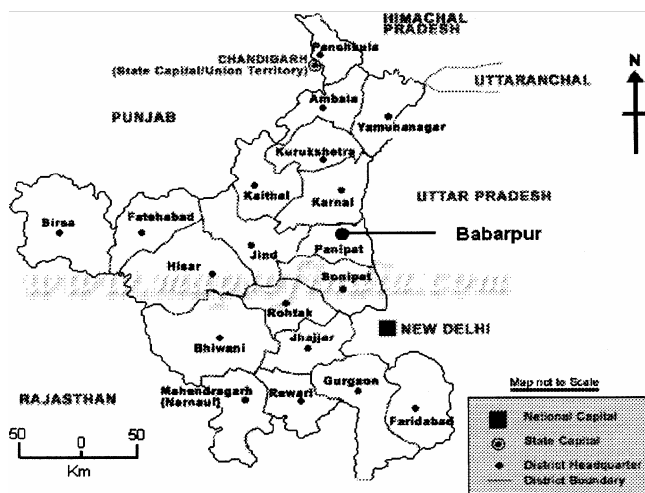


Fig. 1 — Map of Haryana, sampling location at Babarpur

The pH and conductivity were measured immediately after collection of samples.

2.3 Chemical analysis

Concentrations of F^- , Cl^- , NO_3^- and SO_4^{2-} were measured by Ion Chromatograph (DIONEX-100, USA) using analytical column Ion Pac-AS4A-SC 4 mm, anion micro-membrane suppressor ASRS-1, 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate as eluent and triple distilled water as regenerator and atomic absorption spectrophotometric technique was used to measure Na^+ , K^+ , Ca^{2+} and Mg^{2+} , while NH_4^+ ion was measured by indophenol blue method. The concentration of HCO_3^- was estimated from the theoretical relationship between pH and HCO_3^- (ref. 11) as there were no direct measurements available for HCO_3^- . The pH was measured with a digital pH meter (Elico make, Model L1-120) using reference (KCL solution) and glass electrodes standardized with pH 4.00 and 9.2 reference buffers before and after pH determination. Conductivity was also measured with a digital EC-TDS analyzer (Elico, model CM-183).

2.4 Data quality

The quality of data was assessed by ionic balance. The ratio of total anions to that of total cations is an indicator of the completeness of measured parameters. Bicarbonate ion concentrations were included in the anion total. The above ratio in the present study is found to be 0.93 (less than unity), which suggests that some anions were not measured. The missing anions such as organic ions can alter the ratio. The main sources of organic ions in the atmosphere are oxidation of hydrocarbons by vegetation and direct

emission from industrial sources⁶. Linear correlation between sum of anions and cations, significant at the 95% confidence level, was within the range of quantitative ionic balance⁷.

3. Results and discussion

3.1 Chemical composition of rainwater

Volume weighted mean (VWM), minimum, maximum and standard deviation of major ions along with pH and conductivity of rainwater samples collected during summer monsoon season 2003-2005 are presented in Table 1.

The volume weighted mean pH of rainwater was 5.51, which is slightly acidic in nature and varied from 5.02 to 6.86. Figure 2 illustrates the frequency distribution of pH with highest frequency of 35% in the pH range 5.0-5.5. These relatively low values of pH in rainwater suggested the dominance of acidic components. However, 63% of rainwater was alkaline due to dominance of basic components particularly the presence of carbonates and bicarbonates of calcium. The northern parts of India are influenced by natural dust particles blown by winds from the nearby arid desert in Rajasthan. The high specific conductivity ($11.29 \mu S cm^{-1}$) has been found by the dissolution of soil dust also. Kulshrestha *et al.*¹⁰ reported alkaline nature of rainwater in northern parts of India (Delhi) due to heavy loading of particulate matter rich in carbonate and bicarbonates of calcium, which neutralize the acidity. Despite this, the acidity of rainwater could not be fully neutralized and acidic rain (37%) occurred at Panipat due to high concentrations of SO_4^{2-} and NO_3^- released from the aforesaid anthropogenic sources. Acidic events were only observed with low atmospheric buffering potential caused by a heavy rainfall settling dust particles.

VWM concentration of sulphate, calcium and ammonium in rainwater were 95.20, 75.41 and 39.24 $\mu eq/l$, respectively, which were high in comparison with other characteristics. The high average concentration of sulphate could be due to local pollution sources. The air quality at Panipat is poor due to emissions from thermal power plant, oil refinery, fertilizer plant and other small-scale industries. Some pollutants are also transported from the industrial belt located in the central part of India, eastern Uttar Pradesh and its neighborhood, by the winds associated with monsoon systems/trough¹⁴.

Table 1 — Volume weighted mean (VWM) concentration ($\mu\text{eq/l}$), minimum (Min), maximum (Max) and standard deviation (SD) of major ions along with pH and conductivity of rainwater at Panipat

	Cl^-	SO_4^{2-}	NO_3^-	F^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	pH	Cond.
VWA	31.0	95.2	26.6	17.8	39.2	25.9	15.9	75.4	25.2	11.3	5.51	24.4
Max	109.2	241.3	97.9	72.4	85.4	97.8	27.2	317.5	70.0	64.6	6.86	68.8
Min	3.5	28.2	7.2	3.2	14.2	1.7	2.4	19.5	2.9	0.9	5.02	5.8
SD	22	47	18	14	18	19	6	54	16	18	3	16

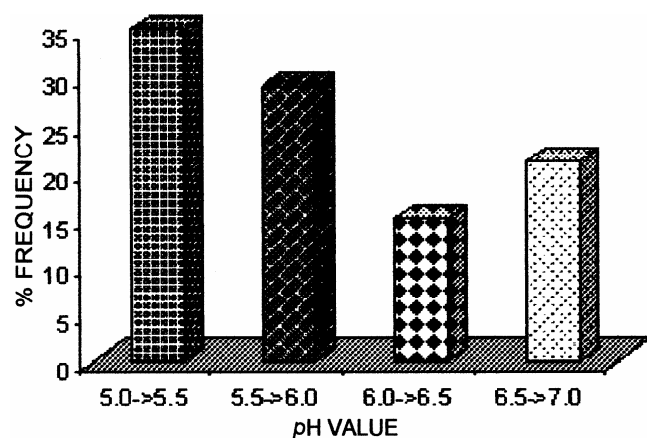


Fig. 2 — Frequency distribution of pH

In terms of average concentration, the ionic abundance in precipitation ($\mu\text{eq/l}$) showed the general trend as $\text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Cl}^- > \text{NO}_3^- > \text{Na}^+ > \text{Mg}^{2+} > \text{F}^- > \text{K}^+ > \text{HCO}_3^-$. Variation in the concentrations of chloride and sodium were not significant. Since precipitation during July - September is mainly due to south-west monsoon originating from Bay of Bengal and Arabian Sea, the composition of precipitation also reflects marine origin. Small fractions of non-marine constituents could be due to the entrainment of atmospheric particulate matter in the precipitation enroute the trajectories of air masses. The predominant source of Cl^- in rainwater is sea spray.

Nitrogen dioxide is emitted into the atmosphere mainly by (i) combustion of fossil fuels and biomass burning; (ii) action of bacteria in the ground; and (iii) oxidation of nitrogen¹⁵. NO and NO_2 will eventually end up as NO_3^- in rainwater, which in the present case is $26.57 \mu\text{eq/l}$. The average concentrations of SO_4^{2-} and NO_3^- at Panipat area were observed nine times higher than that of background hemisphere value of sulphate ($\sim 10 \mu\text{eq/l}$) and nitrate ($\sim 2.8 \mu\text{eq/l}$), respectively¹⁵. Concentration of NH_4^+ at Panipat varied between 14.23 and 85.41 $\mu\text{eq/l}$. Ammonium in precipitation results from ammonia generated by the action of bacteria on nitrogen compounds in the soil, from industrial plants during manufacturing of fertilizers and perhaps mainly from urine. Ammonium

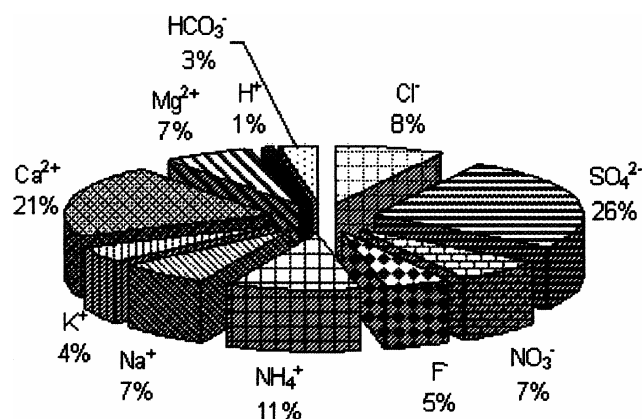


Fig. 3 — Contribution of each ionic species to the total ionic concentrations

ion in rainwater helps in neutralizing the acidic nature caused by H_2SO_4 and HNO_3 .

Average concentrations (VWM) of Ca^{2+} , Mg^{2+} and K^+ in rainwater during monsoon season 2003-2005 were 75.41, 25.23 and 15.87 $\mu\text{eq/l}$, respectively. The high concentrations of Ca^{2+} , Mg^{2+} and K^+ in rainwater are mainly due to high levels of total suspended particles / dusty soil transported from Thar Desert in the west in the neighboring state of Rajasthan. Hence, during the monsoon period, these constituents enter into rainwater by rainout and washout processes. Soil in the northern parts of India is generally dusty, a major contributor to total suspended particulate matter (TSPM) in the air. Kulshrestha *et al.*¹¹ reported highest total suspended particulate pollutant concentrations in summer and lowest in the monsoon while moderate values in the winter. This variation is due to stronger winds entraining large quantities of dry soil in summer and high washout rate during monsoon period.

The relative percentage contribution of each ionic constituent to the total ionic concentration is shown in Fig. 3. The alkaline components (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , H^+ and NH_4^+) contribute approximately 51% of the total ion mass while the remaining are the acidic components (SO_4^{2-} , Cl^- , F^- , NO_3^- and HCO_3^-). The calcium ion accounts 21% of the total ion mass, the highest contribution to the total mass of the cations,

which is due to soil dust. Likewise, sulfate ion, 26% of the total mass and 52% of total mass of anions, is due to industrial emissions. Sulphate contributes maximum concentration (26%) and potassium contributes minimum (4%) to the rainwater-measured ions. On an average, nitrate concentration is low and accounts only 7% to the total ionic concentration. The contribution of magnesium, however, is 7%.

3.2 Marine contribution

To assess the contributions of marine and non-marine origin, sea salt fractions and enrichment factors in the rainwater have been calculated using sodium as reference element with an assumption that all sodium is of marine origin only. These results are presented in Table 2. The ratio of major sea salt components to sodium is remarkably steady in the oceans over the world¹⁷. The ratio values of all species are higher except sea salt suggesting the dominance of non-marine contribution in precipitation. A fraction of non-marine constituents may be due to the entrainment of atmospheric particulate matter in precipitation along the trajectory path of air masses. The ratio of Cl^-/Na^+ in the precipitation samples was found to be equal to that in seawater during the study period. The ratios of $\text{Mg}^{2+}/\text{Na}^+$, K^+/Na^+ , $\text{Ca}^{2+}/\text{Na}^+$, $\text{SO}_4^{2-}/\text{Na}^+$ were found to

be higher than that of seawater. The excess of Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} in rainwater is attributed to non-marine sources such as soil-dust or other anthropogenic sources. Compounds containing Ca^{2+} , Mg^{2+} and K^+ are added to the atmosphere by soil erosion in the form of their carbonate salts⁸.

Table 2 also shows that all components are enriched indicating the absence of marine influence except sea salt. It is interesting to note that the EF of Cl^- is fairly close to unity despite the ocean being far from the observation site. This may probably be attributed to both long-range transport by wind of marine origin and salty soil profile of the region during monsoon period. Table 2 also points out that nearly all species [SO_4^{2-} (97%), Ca^{2+} (93%), K^+ (94%), Mg^{2+} (93%) and Cl^- (6%)] were of non-marine origin. It is, therefore, presumed that the excess SO_4^{2-} is not of marine origin but from industrial sources.

3.3 Determination of chemical sources

Sources of measured rainwater parameters were statistically examined by linear correlation and the results are presented in Table 3. Correlation (r) is considered well if $r > 0.6$ and marginal if $0.34 < r < 0.50$ at 95% confidence level. A strong correlation

Table 2 — Equivalent concentration ratios of ionic components w.r.t. sodium

	Cl^-/Na^+	$\text{Mg}^{2+}/\text{Na}^+$	K^+/Na^+	$\text{Ca}^{2+}/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$
Rainwater	1.26	1.78	1.02	6.26	6.39
Seawater*	1.16	0.227	0.0218	0.0439	0.125
Enrichment Factor	1.08	7.84	46.79	142.60	51.12
Sea Salt Fraction	94%	7%	6%	7%	3%
Non Sea salt Fraction	6%	93%	94%	93%	97%

*Keene *et al.*, 1986

Table 3 — Correlation coefficient of ionic constituents in precipitation

	Cl^-	SO_4^{2-}	NO_3^-	F^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	pH	HCO_3^-
Cl^-	1.00										
SO_4^{2-}	0.35*	1.00									
NO_3^-	0.22	0.51**	1.00								
F^-	0.19	0.18	0.51**	1.00							
NH_4^+	0.02	0.22	0.09	0.11	1.00						
Na^+	0.98**	0.35*	0.22	0.21	0.03	1.00					
K^+	0.50**	0.05	0.23	0.04	0.02	0.43*	1.00				
Ca^{2+}	0.44*	0.37*	0.65**	0.58**	0.11	0.51**	0.15	1.00			
Mg^{2+}	0.31	0.27	0.44*	0.19	-0.04	0.52**	0.52**	0.35*	1.00		
pH	0.37*	-0.49*	-0.10	-0.05	0.04	0.36*	0.34*	0.35*	0.25	1.00	
HCO_3^-	0.48**	0.21	0.04	0.13	0.19	0.18	0.34	0.44*	0.31	0.85**	1.00

Two tail test * Significance < 0.05 ** Significance < 0.01

between Cl^- and Na^+ ($r = 0.98$) was observed, which confirms that ionic concentration of sodium and chloride in rainwater were mostly influenced by marine spray coming from Arabian Sea and Bay of Bengal during monsoon period. Chloride also shows good correlation with Ca^{2+} ($r = 0.44$) and K^+ ($r = 0.50$), which suggests that some portion of chloride may be due to wind blown soil dust. Na^+ , K^+ , Ca^{2+} and Mg^{2+} have good correlation coefficient among them implying that they might have originated from the same source, viz. the soil. NO_3^- was significantly correlated with Mg^{2+} ($r = 0.44$), F^- ($r = 0.51$) and Ca^{2+} ($r = 0.65$) indicating that some nitrate is also in non-acidic salt form. Soil is also the source of nitrate to rainwater, which is present in the atmosphere in coarse mode during rainy season in the form of their corresponding salts, viz. $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$. Sulphate showed correlation with Ca^{2+} , indicating that some portions of sulphate aerosols scavenged by rain are in the form of CaSO_4 . Sulphate, however, showed inverse correlation ($r = -0.49$) with pH value. This implies that increase in the concentration of sulphate is responsible for reduction in pH , hence an increase in rainwater acidity in few cases. SO_4^{2-} and NO_3^- have strong correlation with each other indicating their origin from similar sources. This is due to similarity in their behavior in precipitation as a result of emissions of their precursors, SO_2 and NO_x , responsible for acid rain.

The ratio of SO_4^{2-} to NO_3^- indicates the source of sulphate. In the present case, the ratio was 3.58, which is higher and might be due to strong urban sources besides industrial sources¹⁸. The source of ammonium ion is neither the soil nor the sea. Ammonium is generally correlated with sulphate and nitrate in the form of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . The sulphate to ammonium ratio (2.43) is half of that of the emission ratio (5.7) in Indian regions¹⁴. This shows that a large amount of ammonium emitted is lost by other ways and not through deposition. However, ammonium ion is found in its salt form both in fog and rain at nearby station⁸. No correlation is observed between ammonium and acidic species in this study. Migliavacca *et al.*⁵ have reported that production of F in the atmosphere is due to burning of coal, which is used in thermal power plants. Ali *et al.*⁸ have also reported the same view for their study in fog water at Delhi. In the present study, fluoride show significant correlation with calcium ($r = 0.58$) and nitrate ($r = 0.51$), which indicates that some part of fluoride occurred from the local soil. Being industrialized area,

possible availability of hydrogen fluoride in the atmosphere could not be ignored.

3.4 Factor analysis

Factor loadings for each variable have been calculated by principal component analysis using SPSS PC ++ package (version 7.5 for Windows). In general, factor loadings greater than 0.5 are considered significant in aerosol studies¹⁹. The factor loadings with the variance accounted by the various factors for Eigen value >1 are presented in Table 4. The factor loadings show the data synthesized into four major factors, explaining about 79.4% of the total variation. The division of information into different groups [common factors] can be interpreted as the variables listed within the same factor might have the same origin.

The first factor explains 35.5% of the total variance of Ca^{2+} , F^- , Cl^- , K^+ , Mg^{2+} and Na^+ . The high loading of these aerosols indicates the influence of natural sources like soil and sea. The high loading of these ions in this factor is associated with the influence of natural sources like soil and sea. Norman *et al.*¹⁴ also indicated similar influence of sea-salt loaded marine air from south-east during monsoon for northern Indian region. Apart from the marine influences, a very high loading of bicarbonate is also found in this factor as a byproduct of alkaline carbonates salt such as calcite, dolomite and gypsum⁶. As a matter of fact, Ca^{2+} , and Mg^{2+} are frequently found in soil and dust, which explains the association of these species in the same factor. Wind-blown dust transported from Thar Desert in the west is the source of alkaline soil derived components.

Table 4 — Factor analysis of ionic species

	Factor 1	Factor 2	Factor 3	Factor 4
Ca^{2+}	0.73			
Cl^-	0.84			
F^-			0.50	
H^+		0.77		
F^-	0.73			
K^+	0.60			
Mg^{2+}	0.67			
Na^+	0.84			
NH_4^+			0.55	0.69
NO_3^-		0.64		
SO_4^{2-}		0.86		
Eigenvalue	4.25	2.88	1.40	1.19
% Variance	35.5	24.0	11.7	9.9
Cumulative	35.5	59.5	71.2	81.2

The second factor explains 24% of the total variance, being high loading of SO_4^{2-} , NO_3^- and H^+ , which may be attributed to industrial activities and scavenging process. SO_4^{2-} is derived from anthropogenic activities like oxidation of sulphur dioxide in the atmosphere, emission from thermal power plant and oil refinery, etc. The variance of NO_3^- in this second factor also suggests incomplete combusted exhaust from automobiles and diesel generators/tractors, which were abundant in this area and produce nitrates. Free acidity [H^+] shared high factor loadings with the above mentioned three ions suggesting that the acidity of rainwater is controlled by acid forming ions, i.e. SO_4^{2-} and NO_3^- .

The third and fourth factors account for 21.6% of the total variance in the observations with high loading of F^- and NH_4^+ and this may be linked to biogenic activity and traditional combustion. Emissions of NH_3 and F^- come from both anthropogenic and natural origin, where manure being the largest single source. About 30% of the nitrogen excreted from farm animals is released to the atmosphere from bacterial action on nitrogen compounds in the soil, urine excretion by humans, grazing animals; from industrial sources; from fuel storages; and also due to application of animal waste to the soil. The high NH_4^+ concentration found in rainwater might be related to ammonium gas introduced into the atmosphere mainly by cattle farming (80%), use of fertilizers (17%) and industrial activities⁵. High loading of F^- suggests the contribution of HF acid related to the coal-fired power plant and bricks-kilns.

3.5 Neutralization factor

The relative importance of neutralizing components is visualized and calculated theoretically¹³. In the precipitation at Panipat, the calculated neutralizing factors showed the trend as Ca^{2+} (0.66) > NH_4^+ (0.34) > Mg^{2+} (0.22) > K^+ (0.13). The neutralization factor of Ca^{2+} was maximum, which indicated that Ca^{2+} plays a crucial role in neutralizing the acidic nature.

4 Conclusions

The volume weighted mean pH of rainwater was found to be slightly acidic with an average of 5.51 owing to high concentration of sulphate resulting from industrial emissions. The concentrations of SO_4^{2-} , Ca^{2+} and NH_4^+ were found to be very high. Principal component analysis confirmed that significant fraction of SO_4^{2-} in rainwater is

contributed by industrial sources. The ratio value of Cl^-/Na^+ was found to be equal to that in seawater suggesting that these sea salts are transported over long range during monsoon period. The average concentrations of SO_4^{2-} and NO_3^- were 95.2 and 26.57 $\mu\text{eq/l}$, respectively. Some portions of SO_4^{2-} and NO_3^- in rainwater were found in the form of their salts as CaSO_4 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$. From the neutralization factor analysis, it was found that a high concentration of Ca^{2+} ion plays an important role in maintaining alkalinity of rainwater. Compounds containing Ca^{2+} , Mg^{2+} and K^+ are added to the atmosphere in this region by soil erosion in the form of their carbonates salts. These elements are potentially basic in nature and their presence in high concentrations in rainwater helps in neutralizing the acidic effects.

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